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Spent Caustic Treatment

Industrial Wastewater Treatment
Water Arabia 2015

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Introduction / Contents

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- Spent Caustic Background
- Spent Caustic Treatment Options
- Description of the Zimpro® WAO process
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Spent Caustic Background – Sources

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What is the Spent Caustic?

- Spent caustic is a waste product generated by chemical and petroleum sweetening processes

- Spent caustic is produced during the production of high quality:
  - Ethylene
  - LPG
  - Gasoline
  - Diesel
  - Kerosene
  - Natural Gas

Typical Spent Caustic Constituents

Compound	Concentration
NaOH	1-5 wt%
Carbonates	1-5 wt%
Sulfides	0.5-5 wt%
Mercaptans	0.1-1 wt%
Phenols	0-3 wt%
Naphthenics	0-5 wt%
Chemical O_2 Demand	10-250 g/L

Spent Caustic Background – Classification

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Type	Source	Problem Compounds	Most Significant Treatment Challenges
Sulfidic	Ethylene LPG Scrubbers or Natural Gas	Sulfides Mercaptans	Odor COD
Cresylic	Scrubbing of FCC gasoline washes	Phenols and reduced sulfur	Odor Biodegradability COD
Naphthenic	Scrubbing kerosene, diesel, and jet fuel	Naphthenic compounds, phenols and reduced sulfur	Odor Biodegradability COD

Spent Caustic Background – Hazards

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Why is spent caustic difficult to dispose of?

Safety – Potential H_2S release

Extremely Odorous - Sulfides and mercaptan

Low Biodegradability – BOD:COD ratio often 0.3 or lower

Toxic - Phenols in high concentrations

Foaming – Naphthenic acids in high concentration

Oil – Potential emulsified, free and or dissolved acid oils

High COD - 10,000 to 250,000 mg/l COD

Spent Caustic Treatment – Treatment Options

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What are typical spent caustic disposal options?

Off-site

- Deep well
- Brokering to paper mill or alumina producer
- Recovery of cresylic and naphthenic acids
- Hazardous waste disposal

On-site

- Incineration
- Acid springing followed by Biological Treatment in WWTP
- Biological Treatment in WWTP
- Wet Air Oxidation followed by Biological Treatment in WWTP

Zimpro® Wet Air Oxidation – A Siemens Technology

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World's Leading Supplier of Wet Oxidation Systems

- More than 50 years of experience with wet oxidation system design and construction
- Over 200 wet oxidation systems for a variety of applications

Atofina, Rho Italy

Spent Caustic Treatment – Zimpro® Wet Air Oxidation Technology

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What is the Zimpro® Wet Oxidation process?

- Oxidation reactions occur in the water phase
- Elevated temperature (spent caustic treatment ~110˚ to 260˚ C)
- Elevated pressure (spent caustic treatment ~1 to 90 barg)
- Air provides soluble oxygen for oxidation reactions

Spent Caustic Before and After WAO Treatment

Spent Caustic Treatment – Zimpro® Wet Air Oxidation Process Flow Diagram

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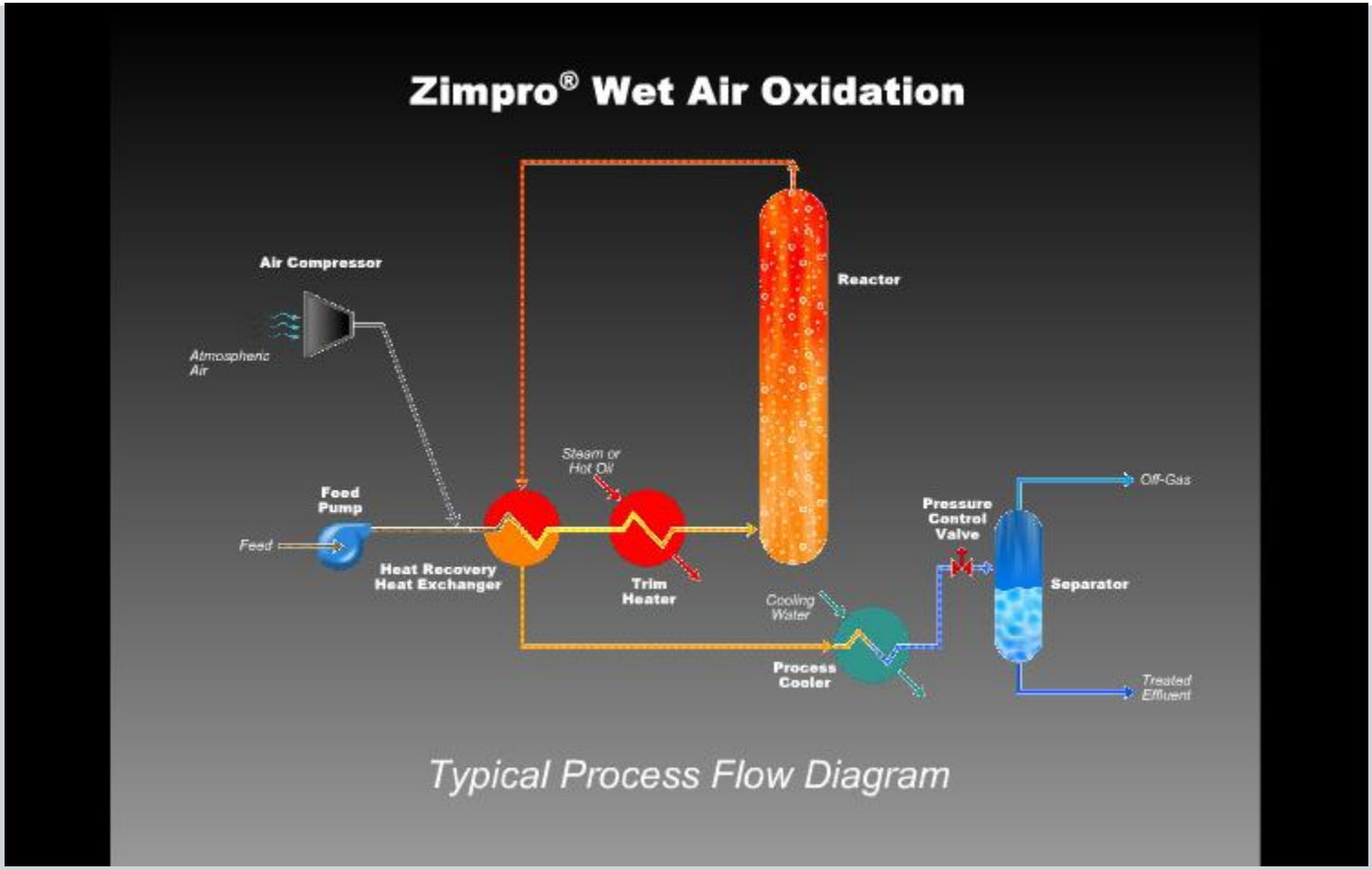

Spent Caustic Treatment – Wet Air Oxidation Treatment Temperatures

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Classification	Temperature (Pressure)	Treatment of Compounds
Low	110 - 150 °C (1.5 – 7 bar)	Reactive Sulfides
Mid	200 -220 °C (20 – 40 bar)	Sulfides, Mercaptans
High	240 -260 °C (50 – 90 bar)	Naphthenic and Cresylic Acids, Sulfides, Mercaptans

Spent Caustic Treatment – Wet Air Oxidation Process

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Wet Air Oxidation Treatment of Spent Caustic

- Destroy reactive sulfides – eliminate odor and H_2S emissions
- Destroy or breakdown complex pollutants (phenols, cresylates, naphthenates)
- Generate effluent that is biodegradable and can be discharged to conventional treatment
- Reduce high COD load sent to downstream treatment

Zimpro® Wet Air Oxidation

Spent Caustic Treatment

- Number one industrial application for the technology
- More than 20 years of experience
- 48 spent caustic treatment systems supplied worldwide

BASF, Port Arthur, Texas

Wet Air Oxidation Treatment of Sulfidic Spent Caustic

Untreated Sulfidic Spent Caustic Characterization

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LPG Spent Caustic Sample

Analysis Results	Units	Reported As	
Chemical Oxygen Demand	mg/L	O_2	62,700
Organic Carbon	mg/L	C	7,260
BOD: COD ratio	---	---	0.3
Sulfide	mg/L	S	17,800
Total Mercaptans	mg/L	CH_3SH	9,880

WAO of Sulfidic Spent Caustic – Reduced Sulfur

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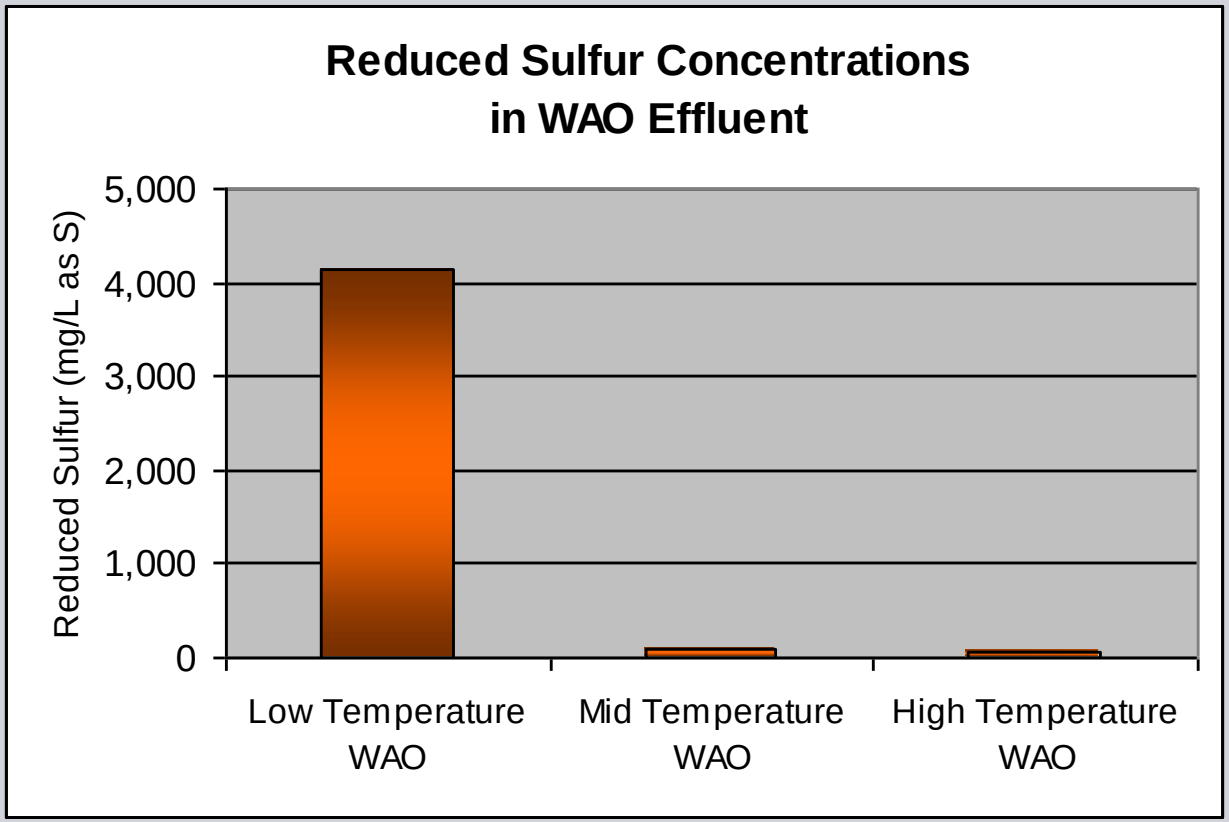

Low temperature WAO effluent- Detectable mercaptans

Mid and high temperature WAO effluent – No detectable mercaptans

WAO of Sulfidic Spent Caustic – Biodegradability

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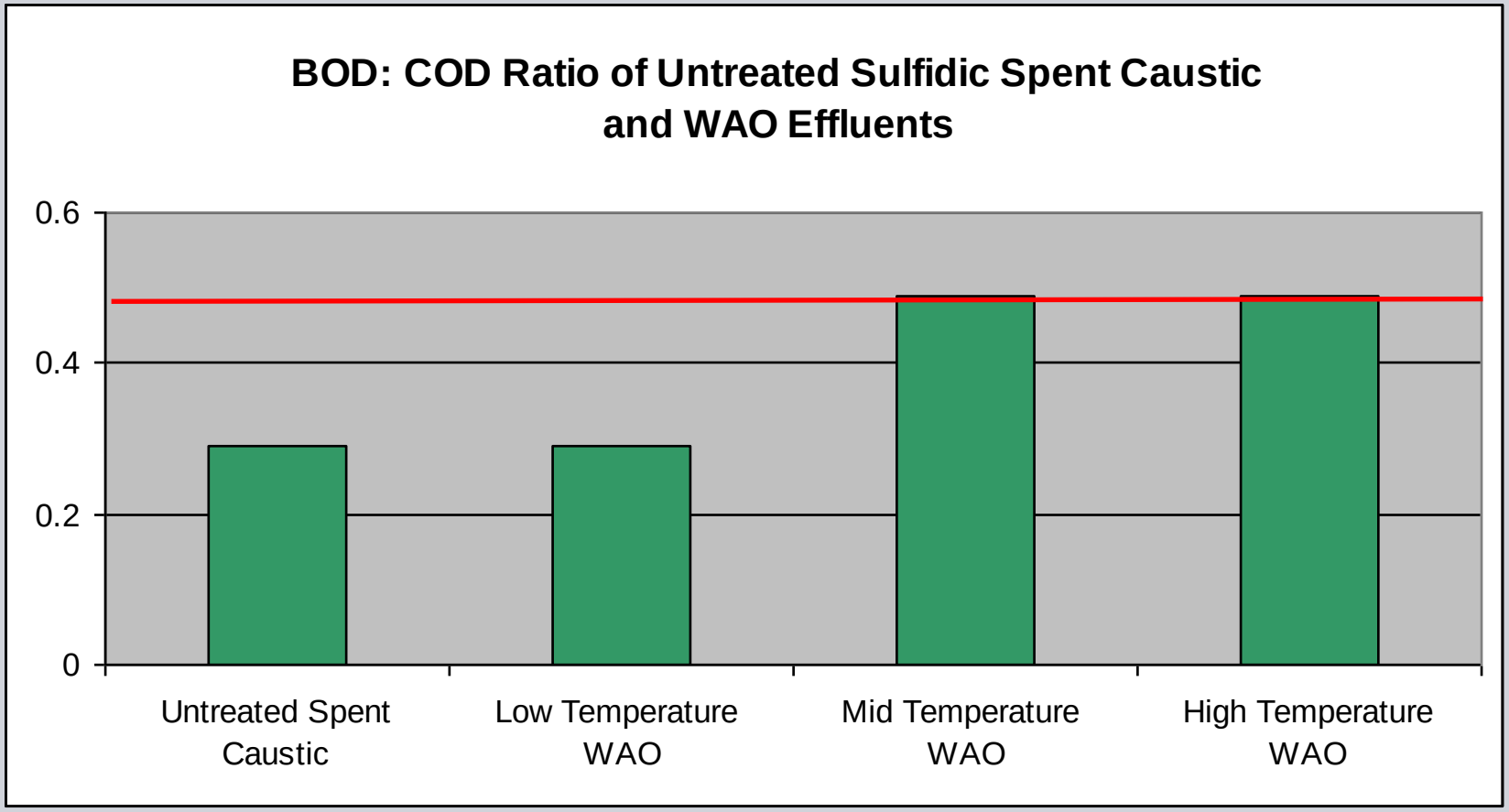

Results Based on 5 Day BOD Test

WAO of Sulfidic Spent Caustic – Biodegradability

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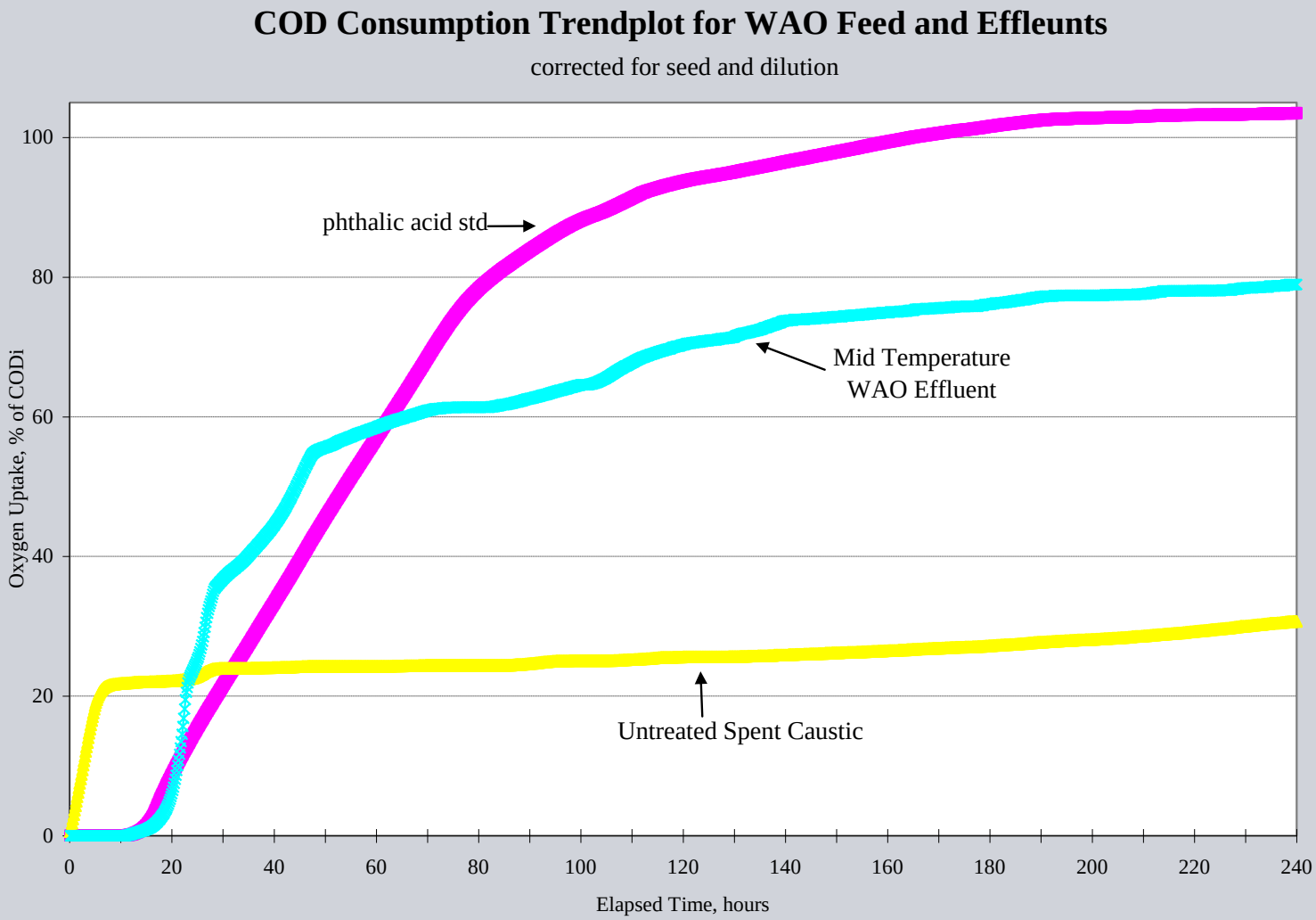

WAO of Sulfidic Spent Caustic – Full Scale Case Study - Chinese Refinery

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System Information

- Mid Temperature WAO System
- Treating Ethylene Spent Caustic
- Located in China

Treatment Results

- Non Detectable Sulfide and Mercaptans
- Readily Biodegradable (>0.6 Biodegradability ratio)
- 93% COD Reduction

			Untreated Spent Caustic	WAO Effluent
Analysis Results	**Units**	**Reported As**		
Chemical Oxygen Demand	mg/L	O_2	42,100	1,420
Biodegradability Ratio	---	---	0.31	0.78
Sulfide	mg/L	S	17,500	<1.00
Mercaptans	mg/L	CH_3SH	<1500	<1
Thiosulfate	mg/L	S_2O_3	2,580	<100

Wet Air Oxidation Treatment of Mixed Refinery Spent Caustic

Treatment of Mixed Refinery Spent Caustic – Untreated Spent Caustic

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Spent Caustics Characterization –

Mixture of Naphthenic and Cresylic Spent Caustic

Analysis Results	Units	Reported As	Analytical Results
Chemical Oxygen Demand	mg/L	O_2	49,300
Organic Carbon	mg/L	C	16,500
Biodegradability Ratio	---	---	0.41
Total Phenols	mg/L	C_6H_6O	1,990
Naphthenic Acids	mg/L	---	18,200

Treatment of Mixed Refinery Spent Caustic - Biodegradability

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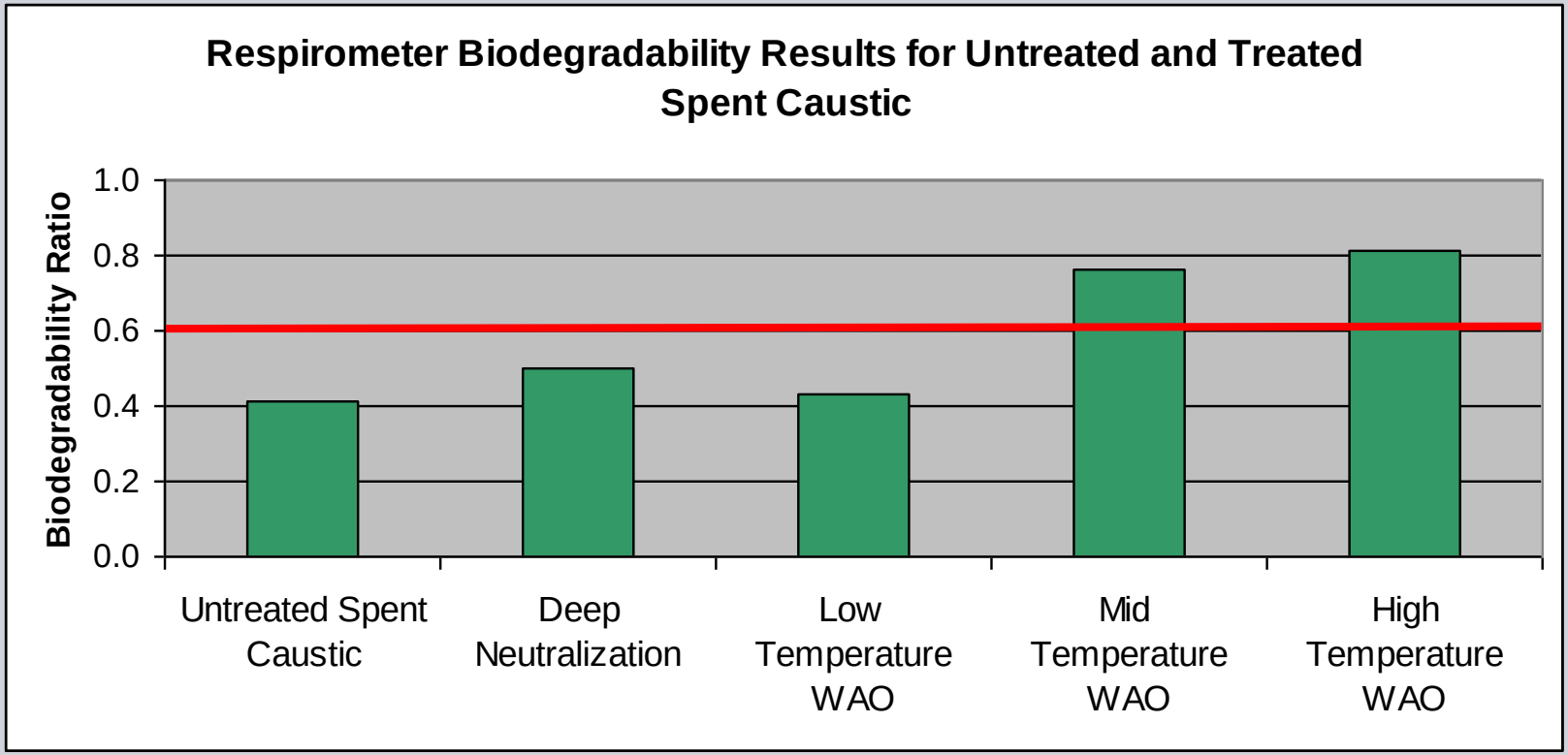

Results Based on 10 Day Respirometer Testing

Wet Air Oxidation
High Temperature WAO Effluent

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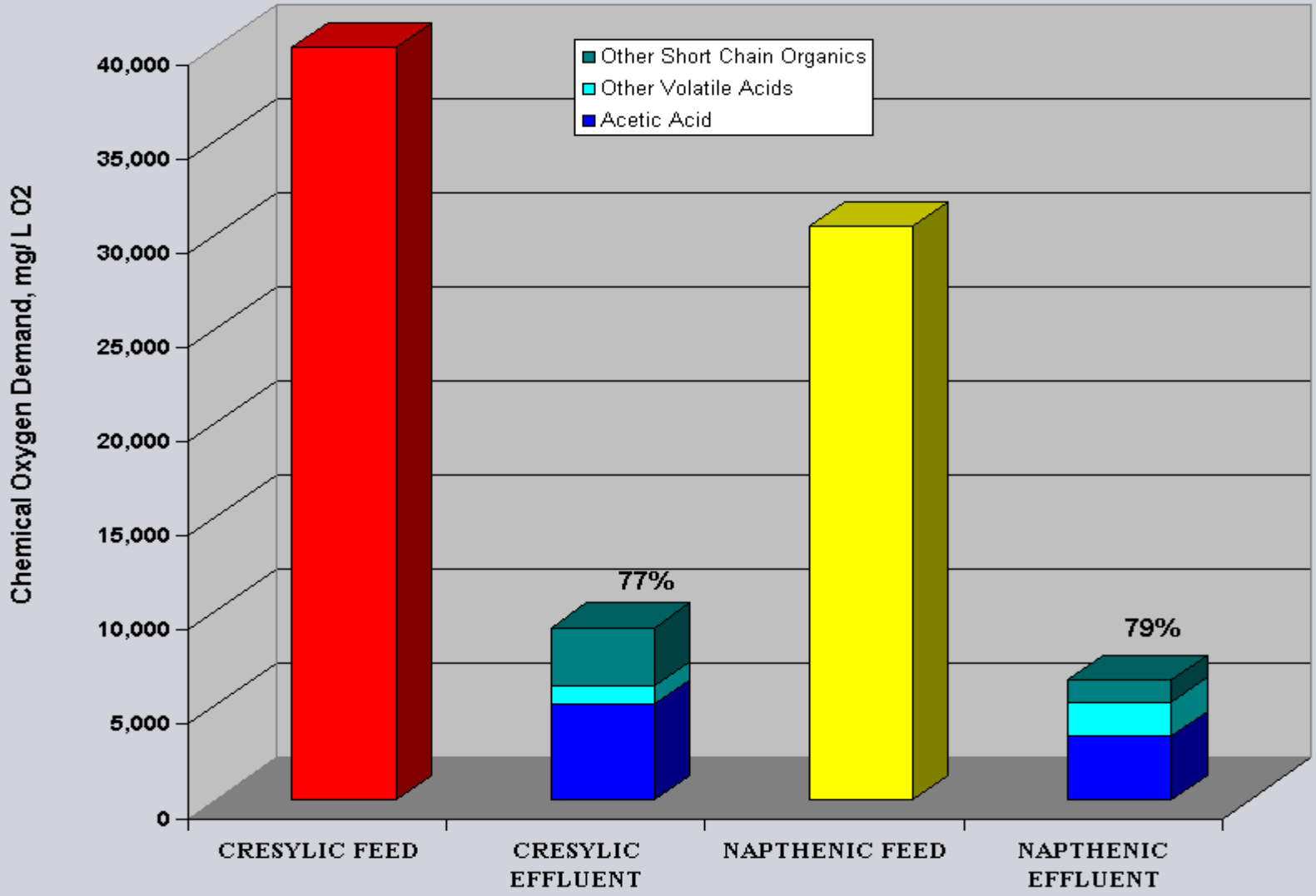

Treatment of Mixed Refinery Spent Caustic - Total Phenols

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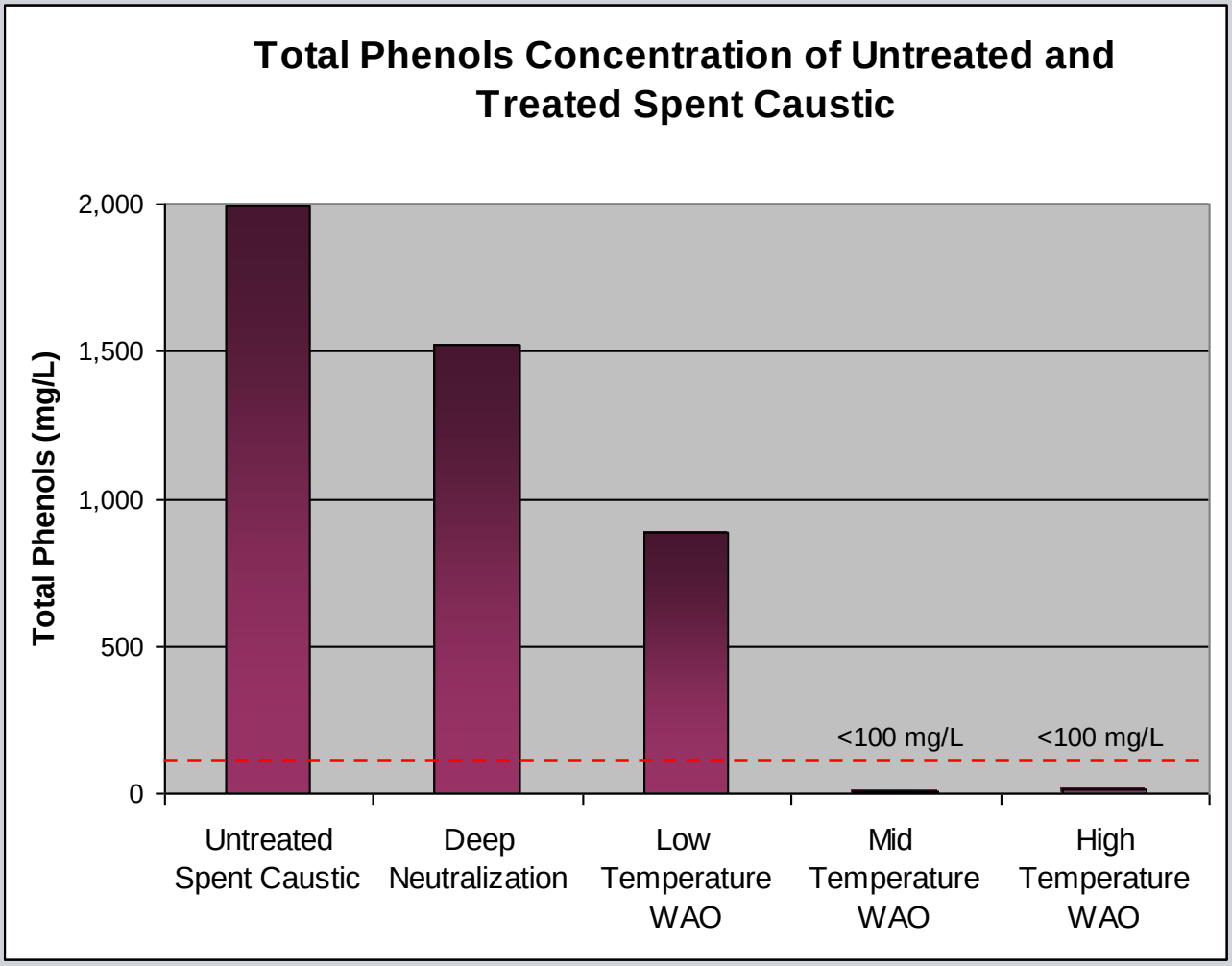

Treatment of Mixed Refinery Spent Caustic – Foaming

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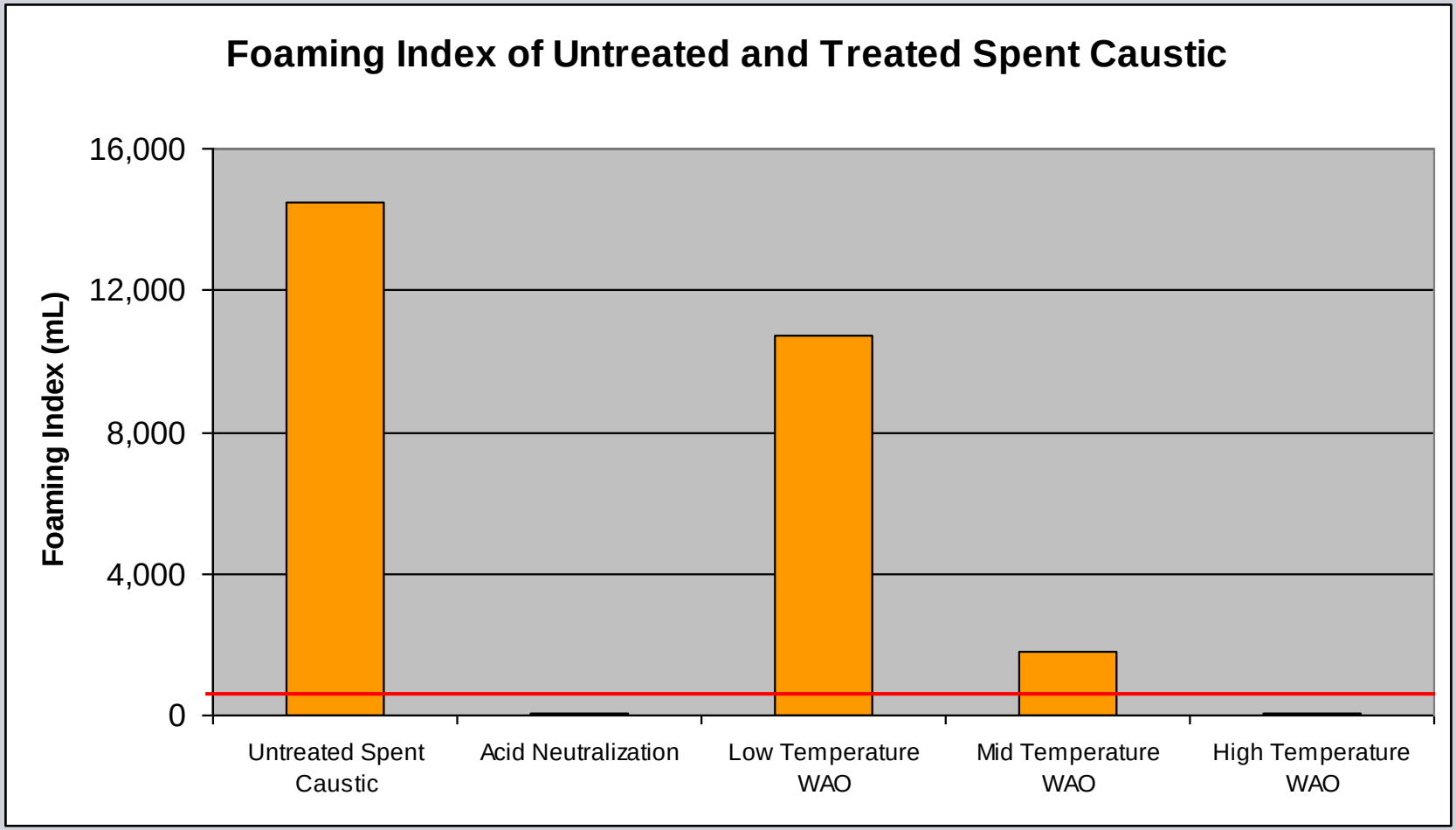

Treatment of Mixed Refinery Spent Caustic - Chemical Oxygen Demand

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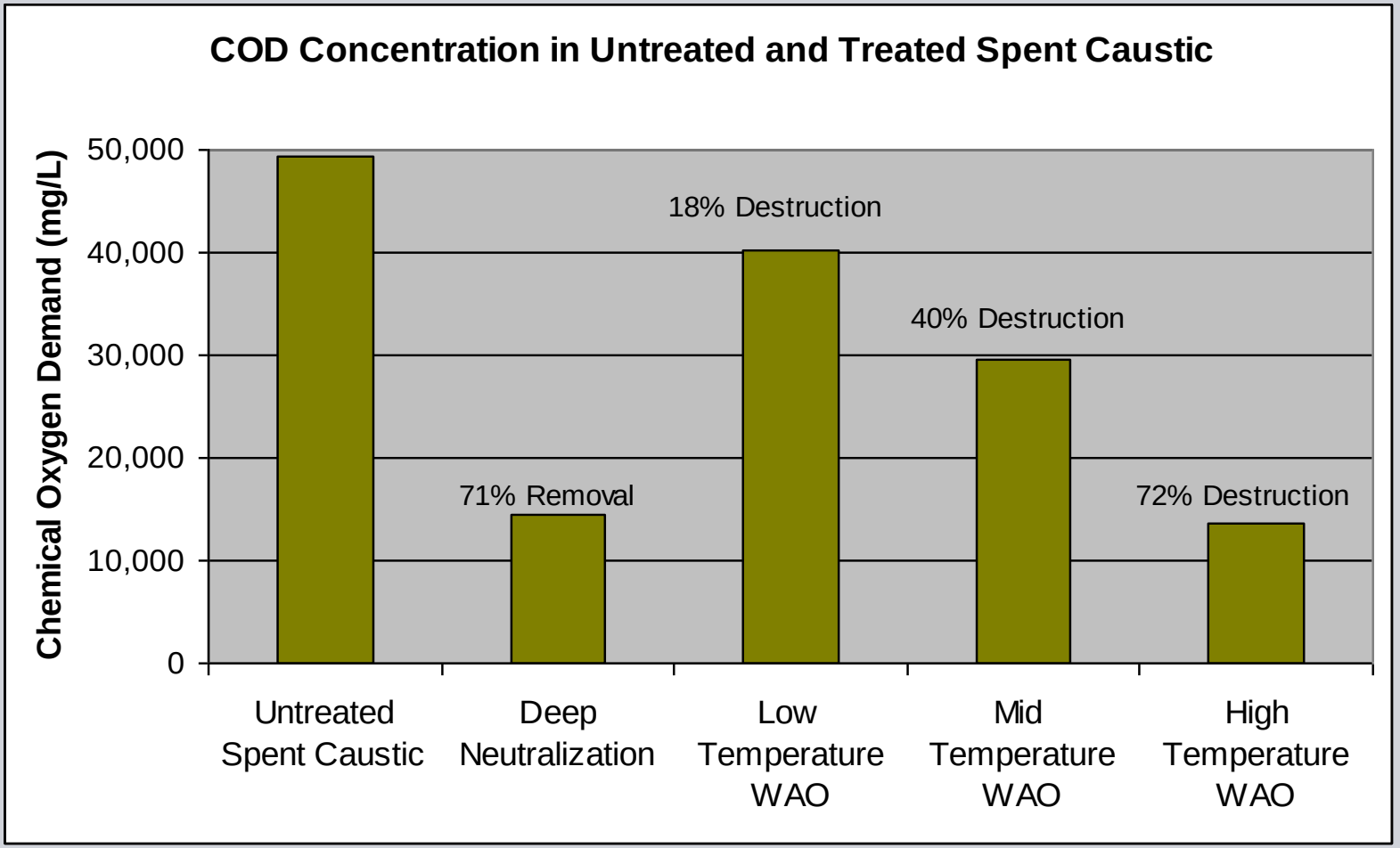

Treatment of Mixed Refinery Spent Caustic - Full Scale Case Study – Indian Refinery

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System Information

- High Temperature WAO System
- Treating Sulfidic, Cresylic and Naphthenic Spent Caustic
- Located in India

Treatment Results

- Non Detectable Sulfide and Mercaptans
- Total Phenols <100 mg/L
- Readily Biodegradable (>0.6 Biodegradability ratio)
- 78% COD Reduction

			Untreated Spent Caustic	High Temperature WAO Effluent
Analysis	**Units**	**Reported As**		
Chemical Oxygen Demand	mg/L	O_2	48,100	10,200
Biodegradability Ratio	mg/L	O_2	<0.1	0.95
Sulfide	mg/L	S	770	<1
Mercaptan	mg/L	CH_3SH	132	<1
Thiosulfate	mg/L	S_2O_3	672	<100
Phenols	mg/L	C_6H_6O	710	<100

Conclusions

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Wet Air Oxidation

- Eliminates safety concerns related to H_2S release
- Eliminates noxious odors
- Produces highly biodegradable effluent
- Destroys difficult to treat naphthenic and cresylic compounds
- Reduces COD load for down stream sent to WWTP

Thank You!

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